



# Evidence of plutonium bioavailability in pristine freshwaters of a karst system of the Swiss Jura Mountains

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## Abstract

The interaction of trace environmental plutonium with dissolved natural organic matter (NOM) plays an important role on its mobility and bioavailability in freshwater environments. Here we explore the speciation and biogeochemical behavior of Pu in freshwaters of the karst system in the Swiss Jura Mountains. Chemical extraction and ultrafiltration methods were complemented by diffusive gradients in thin films technique (DGT) to measure the dissolved and bioavailable Pu fraction in water. Accelerator mass spectrometry (AMS) was used to accurately determine Pu in this pristine environment. Selective adsorption of Pu (III, IV) on silica gel showed that 88% of Pu in the mineral water is found in +V oxidation state, possibly in a highly soluble  $[\text{PuO}_2^+(\text{CO}_3)_n]^{m-}$  form. Ultrafiltration experiments at 10 kDa yielded a similar fraction of colloid-bound Pu in the organic-rich and in mineral water (18–25%). We also found that the concentrations of Pu measured by DGT in mineral water are similar to the bulk concentration, suggesting that dissolved Pu is readily available for biouptake. Sequential elution (SE) of Pu from aquatic plants revealed important co-precipitation of potentially labile Pu (60–75%) with calcite fraction within outer compartment of the plants. Hence, we suggest that plutonium is fully available for biological uptake in both mineral and organic-rich karstic freshwaters.

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## 1. INTRODUCTION

Plutonium is an artificial element found in the environment mainly as a result of atmospheric nuclear weapons tests, nuclear accidents or authorized discharges (Taylor, 2001; Hunt et al., 2013; Alvarado et al., 2014). Pu represents a radiological risk if incorporated through the food chain because of its long biological half-life (Froidevaux et al., 2010a) and emission of high energy alpha-particles.

Physico-chemical properties of plutonium species occurring in freshwaters define its radiological risk for aquatic biota and humans. Pu has complex redox chemistry and can be found under a variety of species in the environment. Consequently, it is challenging to accurately predict its biogeochemical behavior and bioavailability in aquatic ecosystems without precise knowledge of its physico-chemical form and speciation. Environmental Pu can be found simultaneously in both reduced (+III and +IV) and oxidized (+V and +VI) forms, with +IV and +V being the most common species in natural waters (Choppin et al., 1997; Xu et al., 2014). Pu (IV) is generally considered a low-mobility species, tending to precipitate into immobile

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phases, to form intrinsic colloids at significant concentration or to sorb onto organic and inorganic natural colloids at lower concentrations (Santschi et al., 2002; Novikov et al., 2006; Utsunomiya et al., 2007; Chawla et al., 2010). Nevertheless, field experiments have shown that Pu (IV) can be oxidized to Pu (V) in oxic conditions prevalent in the environment (Kaplan et al., 2004). Conversely, Pu (V) is much less sensitive to hydrolysis, has much lower partition coefficients to solid phase and has lower stability constants with organic ligands (e.g. with EDTA) (Katz et al., 1986). Thus, sorbed Pu (IV) can be remobilized as soluble and labile Pu (V) species, which then increase Pu transport and biouptake in aquatic ecosystems (Kaplan et al., 2004; Xu et al., 2014). In addition to the oxidative dissolution of Pu (IV), interactions with naturally-occurring organic matter have critical implications on its sorption and desorption kinetics in the subsurface water environments (Tinnacher et al., 2015). The lability of Pu complexes with fulvic acid (FA) recently demonstrated in laboratory experiments provides new reasons for reconsidering the role of NOM for Pu bioavailability in natural freshwater environments (Cusnir et al., 2014; Cusnir et al., 2016).

Previous work on the use of the DGT technique to determine the lability of the Pu-FA complexes paved the way for direct *in-situ* measurements of the labile environmental Pu (Cusnir et al., 2014; Cusnir et al., 2015). A DGT device for Pu bioavailability measurements contains a polyacrylamide (PAM) gel assembly with a Chelex resin-gel as binding phase, protected with a filter (Davison and Zhang, 1994). The PAM gel layer enables the diffusion of bioavailable Pu species only, which are accumulated in the binding phase for subsequent analysis. Within reasonably short deployment time (2–3 weeks), DGT devices with a large surface area (e.g. 105 cm<sup>2</sup>) accumulate sufficient Pu for accelerator mass spectrometry measurements. Varying PAM gel thicknesses enables probing the dynamics of the molecular interactions of Pu with FA in natural waters *in-situ*, since the greater gel thickness increases the residence time and dissociation of Pu-FA complexes within the gel (Cusnir et al., 2016), thus contributing to the uptake of Pu. To predict the toxic effects of plutonium on aquatic organisms in the presence of dissolved NOM, the *in-situ* assessment of its bioavailability is required.

This paper reports on the use of the DGT and ultrafiltration techniques to determine the bioavailability of Pu in freshwaters of the karst system located in the Swiss Jura Mountains. A previous study on this system demonstrated a higher mobility of <sup>239+240</sup>Pu compared to <sup>241</sup>Am and <sup>137</sup>Cs (Froidevaux et al., 2010b), suggesting that carbonate-rich vadose waters might contain Pu in a soluble, plutonyl-carbonate form similar to [UO<sub>2</sub>(CO<sub>3</sub>)<sub>n</sub>]<sup>m-</sup>. To determine the bioavailable Pu, we need to measure the fraction of total Pu that can be taken up by plant through a diffusion process of free and labile metal species (Davison and Zhang, 1994). Thus, we first used ultrafiltration to reveal the fraction of Pu present as dissolved Pu species of size below 10 kDa. Pu in this fraction can be associated with small organic molecules such as FA. Because Pu-FA complexes were shown in a previous study to be labile in some

extent ( $0.2 < \xi < 0.4$ ) and have dissociation constant in the range of Co<sup>2+</sup> and Fe<sup>3+</sup>-FA complexes ( $k_{dis} = 7.5 \times 10^{-3} \text{ s}^{-1}$ ), Pu-FA complexes will be measurable by the DGT technique. The concentration of Pu measurable by the DGT technique ( $C_{DGT}$  (Pu)) has then been measured *in-situ* using large DGT devices for comparison with the concentration of Pu in the dissolved (<10 kDa) fraction.  $C_{DGT}$  is defined as the bioavailable fraction of Pu, e.g. the fraction that can diffuse through the plant cell wall.

Finally, a mass balance of Pu in plants was obtained using sequential elution that can access the carbonated fraction of Pu deposited on the plant biomass, the extra- and intra-cellular Pu fractions, and the Pu in the residue. This mass balance is necessary to compare the  $C_{DGT}$  concentration to the concentration of Pu in the intracellular fraction because the higher the  $C_{DGT}$  of Pu, the higher the intracellular Pu concentration is expected. These results will help to construct a comprehensive geochemical model of Pu mobility and bioavailability in carbonated mineral and organic-rich waters.

## 2. MATERIALS AND METHODS

### 2.1. Study area

To investigate the speciation of Pu in freshwaters, we chose two distinct aquatic environments located in the Swiss Jura Mountains (Fig. 1). In general, karst systems are characterized by high water permeability, with underground waters highly enriched in carbonates. Their Pu content comes only from the fallout of the atmospheric nuclear bomb tests of the sixties, as demonstrated in a previous study by an average <sup>238</sup>Pu/<sup>239+240</sup>Pu activity ratio of  $0.031 \pm 0.0089$  ( $n = 49$ ) (Froidevaux et al., 2010b).

The first aquatic environment was at the Venoge spring, which is located in the commune of L'Isle, about 20 km northwest of the city of Lausanne, and collects water from a karstic catchment area situated between 700 and 1400 m asl. The hydrological regime of the spring is mixed, with the highest flow rate in April-May (up to 7.50 m<sup>3</sup> s<sup>-1</sup>) and the lowest in the summer period (down to 0.01 m<sup>3</sup> s<sup>-1</sup>). The pH of the water varies between 6.5 and 7.5; at a temperature of ca. 7–8 °C, water is saturated with oxygen and CO<sub>2</sub>. Water of this mineral spring is oxic (Eh 490 mV NHE), carbonate-rich, and has a low NOM content (1 ppm at most). Detailed physico-chemical parameters of the water, as well as the precipitation regime during the sampling and field measurements campaign are given in the [Supplementary Information \(SI\)](#).

The second environment was the Noiraigue Bied brook, which is located at the Vallée-des-Ponts site at 1000 m asl. The complex watershed of the valley is formed by densely drained peat bogs and a river (Grand Bied), which collects atmospheric waters from the catchment and flows into the karstic sinkhole, giving rise to the Noiraigue spring at a distance of 4 km and an altitude of 736 m. The hydrological regime of the brook is strongly dependent on precipitation, with a lowest flow rate of 0.03 m<sup>3</sup> s<sup>-1</sup> and a highest flow rate of 4.5–6.0 m<sup>3</sup> s<sup>-1</sup>. The pH of the water is ca. 6.5–7.5, the temperature varies from 0 °C in the winter season to

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